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QUARTERLY REPORT

GTI PROJECT NUMBER 20916

Modeling of Microbial Induced Corrosion on Metallic Pipelines Resulting from Biomethane and the Integrity Impact of Biomethane on Non-Metallic Pipelines

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List Activities/Deliverables Completed During Reporting Period

		SCH Date	CMPL Date
Task #3	Lab Evaluation of Microbial Corrosion	03/31/2011	In Progress

- Filter test to resolve cell contamination issue

Task #8:	Perfom Bounded Testing	6/30/2011	In Progress

- Completed the construction of gas sampling equipment and dry run.
- Finalized gas sampling process and the schedule.
- Natural gas saturation test is ongoing.
- Comparative testing-baseline without gas exposure is ongoing.

Technical Status

Task 3 - Lab Evaluation of Microbial Corrosion under Simulated Field Conditions

Some unexpected technical challenges were encountered in this quarter. The challenge in Task 3 is that the bacteria in one cell always find a way to migrate to another cell, which is supposed to be kept sterile during the experiment. Many methods and procedures to sterilize and assemble the unit have been tested, modified, and tested again. The root cause has been narrowed down to a few possible contamination sources, but additional time is needed to resolve this issue before Task 4 (data collection) begins.

We have tested different sterilization methods including sonication, wet autoclave, dry autoclave, UV, SSDS (a sporicidal agent), acetone, and various combinations. Different components in the cells were sterilized in a variety of ways. We also tested different ways to assemble the cells after sterilization with an attempt to minimize the assembly steps involved post sterilization. Each step of sterilization and assembly of cell components was verified, and found that both cells were maintained sterile before bacteria inoculation. However, after inoculation in anode cell, the cathode cell exhibits bacterial growth after a few days. It happens that bacteria in the anode cell migrates into cathode cell through a bridge tube equipped with membrane filter.

The filter tests include filters from different manufacturers with pore sizes ranging from 0.1 to 0.45 µm. The way the filters were installed in bridge tube between two cells was also studied. Filter failure can be caused by various reasons, such as filter damage during sterilization, filter defects, or medium circulation in anode cell which may generate some pressure on the filter and result in failure.

An experiment was performed to compare four pre-sterile filters from different vendors. One flask (180 ml medium) was inoculated with bacteria and connected to another flask with no inoculation. The connection tube was equipped with various filters. The flasks were incubated at 30°C for two weeks, without agitation, in a slightly inverted position to prevent air pockets in the silicon tubing from forming.

The medium in the uninoculated flask with Millipore Millex-VV PVDF 0.1 µm filter maintained clear after two-week incubation, though the precipitation started to show up after 10 days. The medium in uninoculated flasks with Pall Acropak 1000 Supor membrane 0.8/0.2µm filter capsule also maintained clear after two-week incubation, though the mold growth was visible after 12 days. The streak plating performed on the culture medium in both flasks confirmed that there was no bacteria growth in the uninoculated flask equipped with above two filters. Another experiment confirmed that the precipitation in the flasks can be the result of contact between the rubber stopper and the culture medium.

A similar experiment was set up in attempt to confirm the results from the first experiment and to identify more filter candidates. The filters include pre-sterile disfilter, pre-sterile medium filter capsule, and a membrane filter steriled with an autoclave. The bacteria growth in the uninoculated flasks was confirmed by streak plating after 20 days of incubation. The results indicated that four types of filter (Whatman Anotop 25 Aluminum oxide filter, Pall AcroPak 20 Fluorodyne II membrane, Pall Acropak 1000 Supor membrane capsule, and Pall Acropak 400 Fluorodyne II membrane capsule) successfully blocked microbial migration from inoculated flask to uninoculated flask. Whatman Anotop 25 Aluminum oxide filter was the first to be tested in two-cell electrochemical cell system.

Anotop 25 Aluminum oxide filter in two cell system

Two cells of the electrochemical system were connected by an Anotop 25 Aluminum oxide filter (pre-sterile, 0.02 µm nominal pore size), and equipped with anode, cathode, and various probes (temperature, pH, reference, and counter). Both cells filled with 2 L of medium, and the anode cell was inoculated with the bacteria consortium. The current and potential between cathode and anode was monitored via a Multielectrode Analyzer, and the corrosion rate of the anode was measured using linear polarization resistance (LPR) through a Potentiostat.

After 36 hours, there was visual biofilm present on the cathode in the uninoculated cathode cell; however, the medium turbidity was not at the same concentration as the inoculated anode cell. Cathode and anode potential difference was maintained in the first nine days even with an increasing medium turbidity and bacteria growth in the cathode cell. The potential difference between anode and cathode was reversed after nine days of incubation. The results indicated that Anotop 25 Aluminum oxide disc filter was not able to stop bacteria migration from anode cell to cathode cell in the two-cell electrochemical system. If the migration is due to limited filering capacity of disc filter, a medium filter capsule with large filter capacity such as Pall Acropak 1000 Supor membrane capsule may help improve the effectiveness of stopping bacteria migration from one cell to another. Another possible reason for bacteria migration through the filter disc is that the negatively charged bacteria were pulled to the cathode cell by the external current/potential applied by measuring the instrument. New types of filters or other solutions will be applied in next quarter to resolve the contamination issue.

Task 8 - Perform Bounded Testing to Generate a Strong Example Data Set

Significant progress has been made in this quarter on construction of biogas collection equipment. The equipment was assembled and a successful dry run was conducted.

The gas connectivity was completed for the saturation test setup. A leak check and dry run was conducted before the saturation test. The operating parameters, such as temperature control and gas flow rate were finalized. The first batch of saturation tests with natural gas was started on April 21, 2011, and the gas saturation progress was monitored by analyzing the gas components absorbed in the test samples (via Head Space Testing). The saturation test will be stopped after the gas components become stabilized in the test samples.

Baseline comparative tests were completed on hardness and dimensional measurements for the three test materials (SBR, NBR, and MDPE). The MDPE samples for PENT (ASTM F1473 Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins) have been put on test.

Protocol for Biogas Collection

The protocol was revised and is shown in Figure 1. Assembly of thecompressor skid was completed, see Figure 2. A successful dry was conducted to verify the protocol before collecting gases in the field. A site trip to collect raw and processed gases has been scheduled for the week of June 20, 2011.

Test Specimens

The test specimens were prepared for the natural gas saturation test, see Table 3 for the specimen sizes and numbers. The rubber samples were cut from the rubber sheet material to size. The plastic test specimens were machined to size from molded plaques. The tensile specimens were prepared by die cut (ASTM D638 Type IV). The compression test samples will be die cut from the 5.7"×2.25"×0.125" plaques after the gas saturation test. To perform hardness and compression test for SBR and NBR, the specimens with 0.125" thickness will be stacked to the requried sample thickness (0.25" for hardness and 0.5" for compression) according to ASTM D2240 and ASTM D575. The dimensions for the PENT test (ASTM F1473 Standard Test Method for Notch Tensile Test to Measure the Resistance to Slow Crack Growth of Polyethylene Pipes and Resins) are 1.97"×0.98"×0.25".

The surface of the test specimens were cleaned with isopropyl alcohol, rinsed with water and dried in air after sample preparation. The specimens were marked by attaching a pin.

Gas Saturation Test

Figure 3 shows the gas saturation test sytem. It consists of a main pressure vessel and a secondary vessel holing the head space samples. The test specimens were set on to the test cage and loaded into the pressure vessels, see Figure 4 and Figure 5 for the specimens in the main and secondary vessel respectively.

The vessels were purged with natural gas to get rid of the air and then a slow flow rate of 0.05 cc/min (0.18 cubic inches per hour) was maintained during the saturation test. The main vessel was purged again with natural gas per week in order to refresh the gas.

The head space samples in the secondary vessel were taken periodically to monitor the gas saturation progress. One sample of each test material (SBR, NBR, and MDPE) was taken at a time, and the samples were then analyzed by gas chromatography (GC) to determine the gas components that have been absorbed into the test specimens. The head space test results during the natural gas saturation test (up to 1176 hours) are shown in Figure 6 through Figure 14.

Comparative Test

Hardness

Hardness testing was performed using a shore hardness testing apparatus. The test method being used is ASTM D2240. An average of five (5) measurements on three (3) replicates were recorded. Results to date are shown in Table 6. There were only two (2) replicates measured for the MDPE material, because it is not necessary to cut out compression samples from the substrate. This gives more area to perform the hardness measurements.

Dimensional Change

The baseline measurements were taken on the specimens for measuring dimensional change before saturation test. The specimen surface was slightly scribed to draw lines along X and Y direction, see

Figure 15 and the positions (x, y) of P_1, P_2 and P_3 were measured using optical microscope. The measurements were taken three times on each specimen and the specimen was repositioned before taking the measurements to obtain the repeatability of the measurements. The distance of P_1P_2 and P_2P_3 were calculated as the baseline dimensional measurements for X and Y directions respectively, see Table 4. Five data points were taken at the center of each specimen to obtain the average thickness (dimension in Z direction), see Table 5.

The dimensional measurements will be repeated on the test specimens after the saturation test to calculate the dimensional change before and after gas saturation.

Table 1. The Tested Filters and Their Characteristics

Manufacturer	Materials	Diameter (mm)	Pore Size (μm)
Millipore Millex-VV	PVDF membrane, disc	33	0.1
Electron Microscopy Services	Surfactant free cellulose acetate (SFCA), disc	26	0.2
Pall Acropak 1000	Supor membrane, in housing	69	0.8/0.2
Pall Gelman	Acrodisc HT Tuffryn membrane, disc	25	0.45

Table 2. Summary of Filter Test Results

				Visual inspection			Streak plate
Manufacturer	**Materials/Model**	**Filter Diameter (mm)**	**Pore Size (μm)**	**One week**	**Two weeks**	**20 days**	**20 days**
Whatman	Anotop 25 Aluminum oxide	25	0.02 (nominal)	Clear with some precipitation	Clear with some precipitation	Clear with some precipitation	**No Growth**
Pall	AcroPak 20 Fluorodyne II membrante	55*	0.1	Clear with some precipitation	Slight turbid with some precipitation (12 days)	**Turbid with some precipitation**	**No Growth**
Pall	Acropak 1000 Supor Membrane capsule	45*	0.8/0.2	Clear with some precipitation	Slight turbid with some precipitation (12 days)	**Turbid with some precipitation**	**No Growth**
Pall	Acropak 400 Fluorodyne II Membrane capsule	45*	0.1	Slight turbid with some precipitation	Turbid with some precipitation	**Turbid with some precipitation**	**No Growth**
Pall	Pall Durapore PVDF membrane	22	0.1	Clear with some precipitation	Turbid with some precipitation (9 days)	Turbid with some precipitation	Growth
Pall	Acropak 500 Supor Membrane capsule	45*	0.1/0.1	Slight turbid with some precipitation	Turbid with some precipitation	Turbid with some precipitation	Growth
No filter, no inoculation negative control	na	na	na	Clear with some precipitation	Clear with some precipitation	Clear with some precipitation	No Growth

* estimated filter diameter using ruler, no manufacturer data available

Table 3. Summary of the Test Specimens for Natural Gas Saturation Test

Length×Width (inch)	Thickness (inch)	Test	NBR	SBR	PE2708
1×1	0.25	Dimensional Change	NA	NA	6
	0.125		6	6	NA
5.75×2.25	0.25	Hardness	NA	NA	2
	0.125	Hardness & Compression	4	4	NA
2×1.625	0.125	Hardness (Out Gas)	6	6	NA
4.5×0.75	0.125	Tensile	8	8	NA
	0.16		NA	NA	7
1.97×0.98	0.25	Slow Crack Growth	NA	NA	6
0.25×0.25	0.25	Head Space	NA	NA	30
0.5×0.5	0.125		28	28	NA

Table 4. Dimensional Change Baseline Measurements (X and Y Direction)

Materials	Spciment #	Measurements									
		X (P_1P_2)					Y (P_2P_3)				
		1	2	3	AVG	STDEV	1	2	3	AVG	STDEV
SBR	1	13.317	13.332	13.340	13.329	0.012	12.962	12.948	12.964	12.958	0.009
	2	13.097	13.098	13.104	13.099	0.004	13.464	13.473	13.483	13.474	0.009
	3	13.381	13.384	13.371	13.379	0.007	13.162	13.156	13.147	13.155	0.008
	4	12.959	12.941	12.945	12.948	0.009	13.642	13.634	13.636	13.637	0.005
	5	13.277	13.292	13.273	13.281	0.010	13.387	13.386	13.366	13.380	0.012
	6	13.261	13.249	13.256	13.255	0.006	13.037	13.033	13.035	13.035	0.002
NBR	1	12.462	12.457	12.462	12.460	0.003	13.211	13.225	13.231	13.223	0.010
	2	13.034	13.044	13.043	13.040	0.005	13.083	13.103	13.110	13.099	0.014
	3	13.071	13.073	13.067	13.070	0.003	13.361	13.377	13.392	13.377	0.016
	4	12.968	12.979	12.986	12.978	0.009	13.370	13.375	13.380	13.375	0.005
	5	13.488	13.480	13.489	13.486	0.005	13.130	13.140	13.154	13.141	0.012
	6	13.188	13.202	13.208	13.199	0.010	13.023	13.040	13.039	13.034	0.010
MDPE	1	12.855	12.859	12.853	12.855	0.003	12.614	12.608	12.607	12.610	0.004
	2	12.645	12.633	12.654	12.644	0.011	12.821	12.796	12.826	12.814	0.016
	3	12.469	12.471	12.466	12.469	0.003	12.829	12.833	12.838	12.834	0.004
	4	12.568	12.576	12.566	12.570	0.005	12.795	12.790	12.774	12.787	0.011
	5	12.497	12.493	12.501	12.497	0.004	12.379	12.355	12.347	12.360	0.017
	6	12.657	12.667	12.659	12.661	0.005	12.344	12.339	12.346	12.343	0.004

Table 5. Dimensional Change Baseline Measurements (Z Direction)

Materials	Specimen #	1	2	3	4	5	AVG	STDEV
SBR	1	6.398	6.388	6.385	6.392	6.388	6.390	0.005
	2	6.399	6.39	6.396	6.4	6.392	6.395	0.004
	3	6.403	6.407	6.396	6.393	6.394	6.399	0.006
	4	6.400	6.388	6.392	6.388	6.381	6.390	0.007
	5	6.399	6.398	6.407	6.408	6.401	6.403	0.005
	6	6.400	6.383	6.384	6.395	6.388	6.390	0.007
NBR	1	2.986	3.006	2.994	2.999	2.986	2.994	0.009
	2	3.437	3.428	3.429	3.476	3.444	3.443	0.020
	3	3.102	3.112	3.109	3.104	3.104	3.106	0.004
	4	3.082	3.093	3.09	3.097	3.092	3.091	0.006
	5	3.092	3.095	3.109	3.093	3.093	3.096	0.007
	6	3.435	3.435	3.462	3.437	3.471	3.448	0.017
MDPE	1	3.370	3.36	3.373	3.375	3.375	3.371	0.006
	2	3.352	3.356	3.376	3.353	3.364	3.360	0.010
	3	3.369	3.368	3.371	3.373	3.36	3.368	0.005
	4	3.386	3.381	3.381	3.372	3.379	3.380	0.005
	5	3.358	3.347	3.365	3.365	3.365	3.360	0.008
	6	3.389	3.391	3.373	3.396	3.39	3.388	0.009

Table 6. Hardness Data

Material	Hardness Sample 1	Hardness Sample 2	Hardness Sample 3
SBR	68, Shore A, Stack of 2	68, Shore A, Stack of 2	67, Shore A, Stack of 2
NBR	69, Shore A, Stack of 2	70, Shore A, Stack of 2	70, Shore A, Stack of 2
MDPE	33, Shore D, 1.2 kg Load	33, Shore D, 1.2 kg Load	N/A

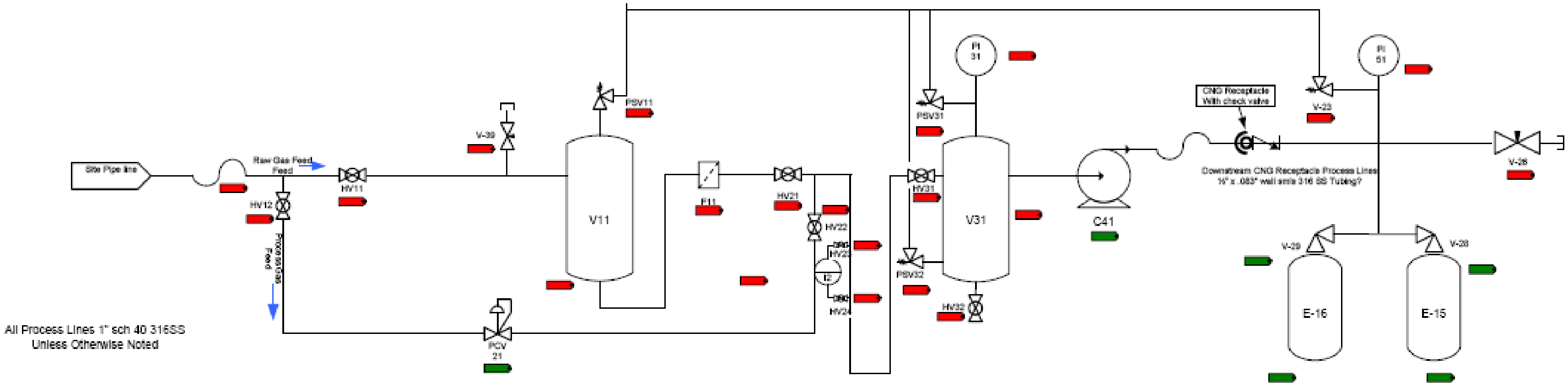

Figure 1. Biogas Collection Schematic (Updated)

Figure 2. Biogas Collection Skid with Compressor

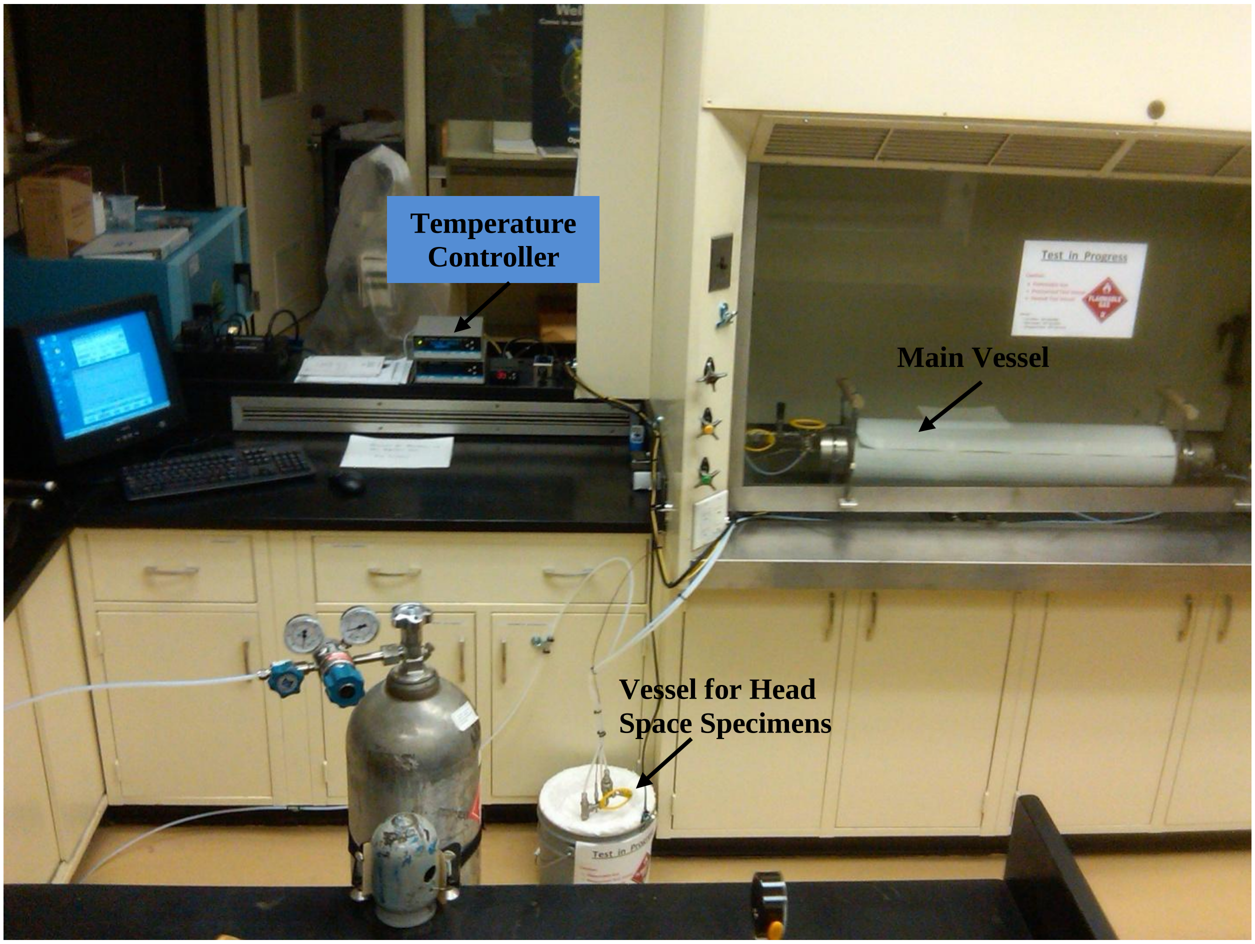

Figure 3. Gas Saturation Test System

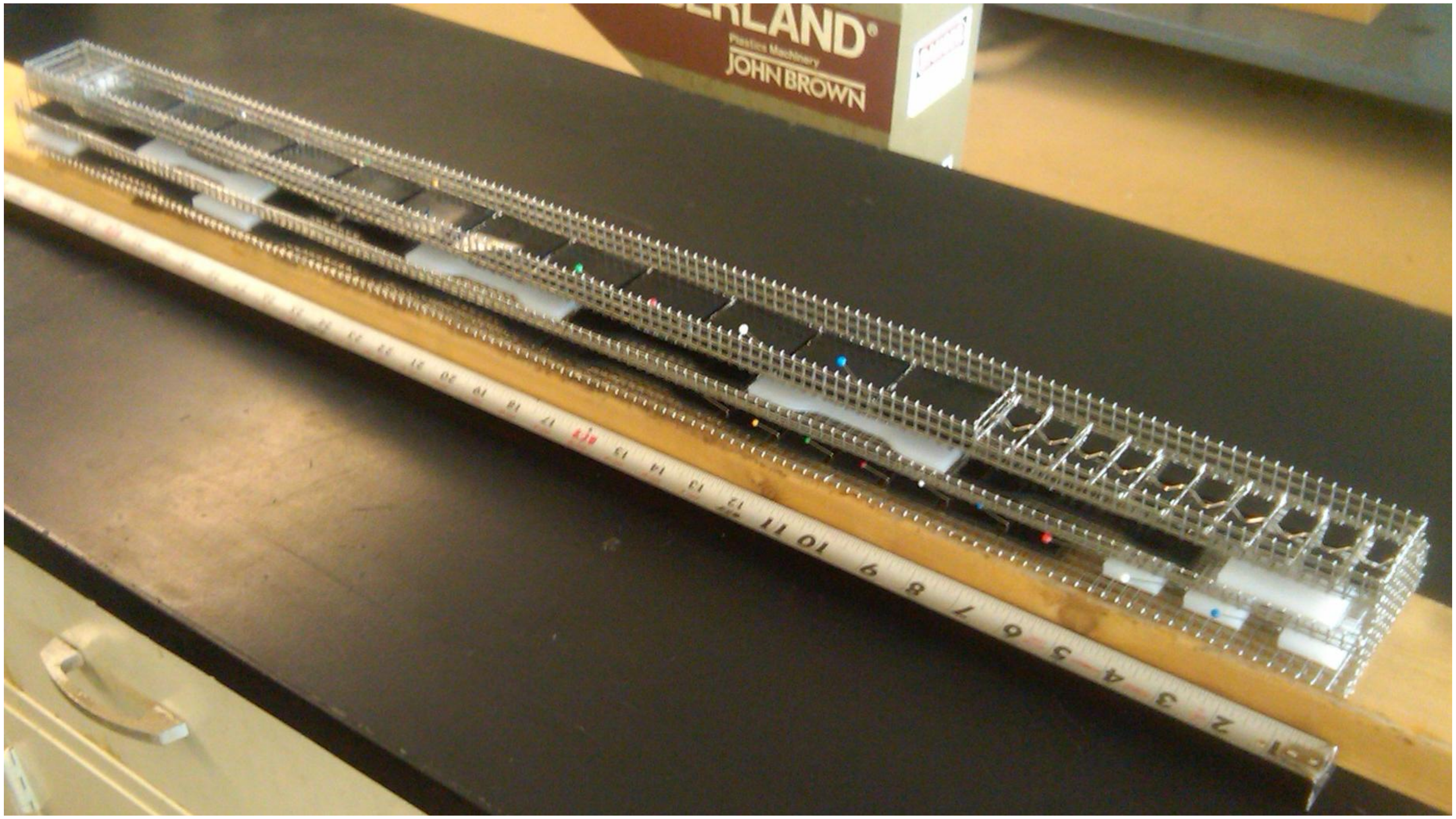

Figure 4. The Test Specimens in the Cage before Loading into the Pressure Vessel

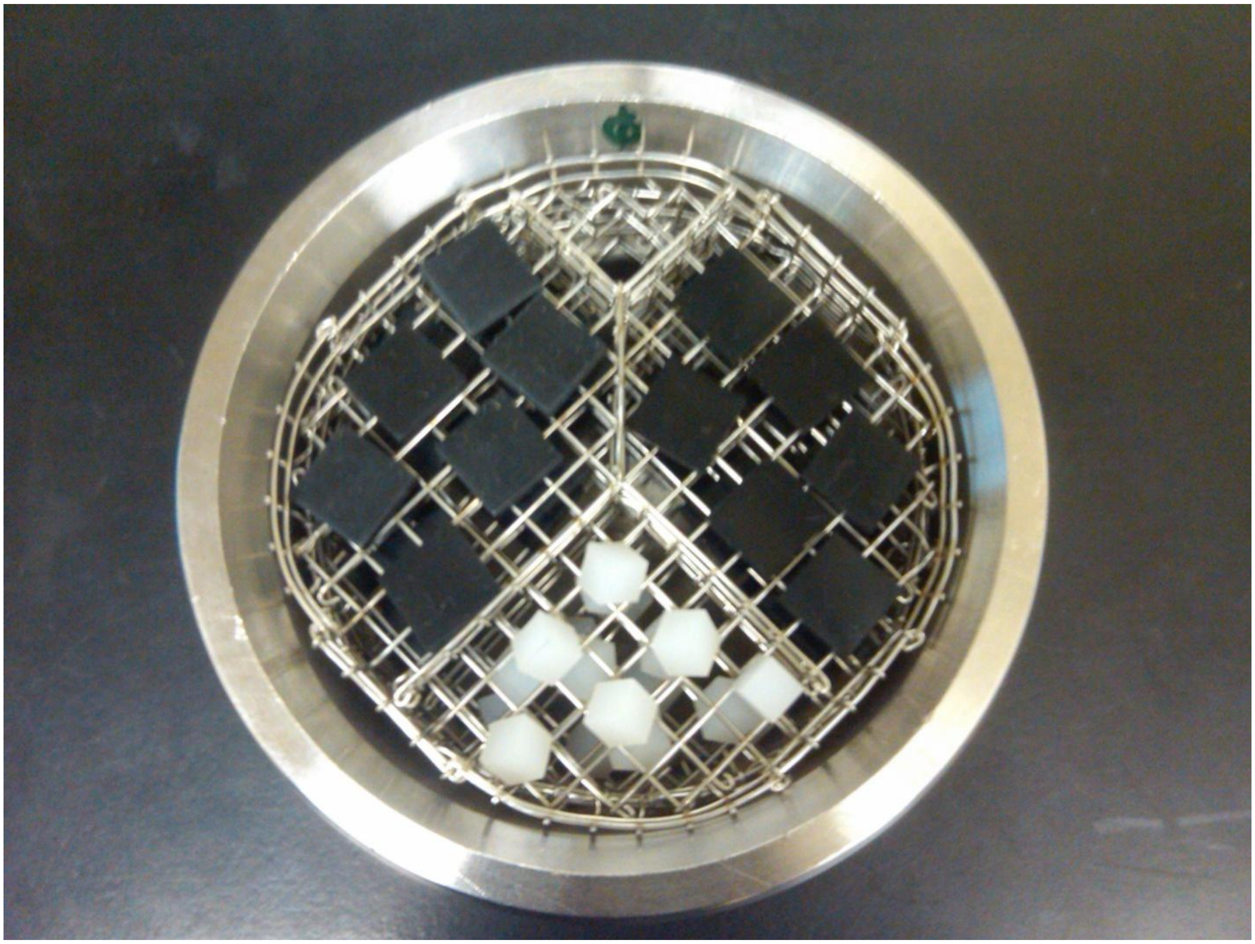

Figure 5. Head Space Test Specimens Loaded in the Vessel

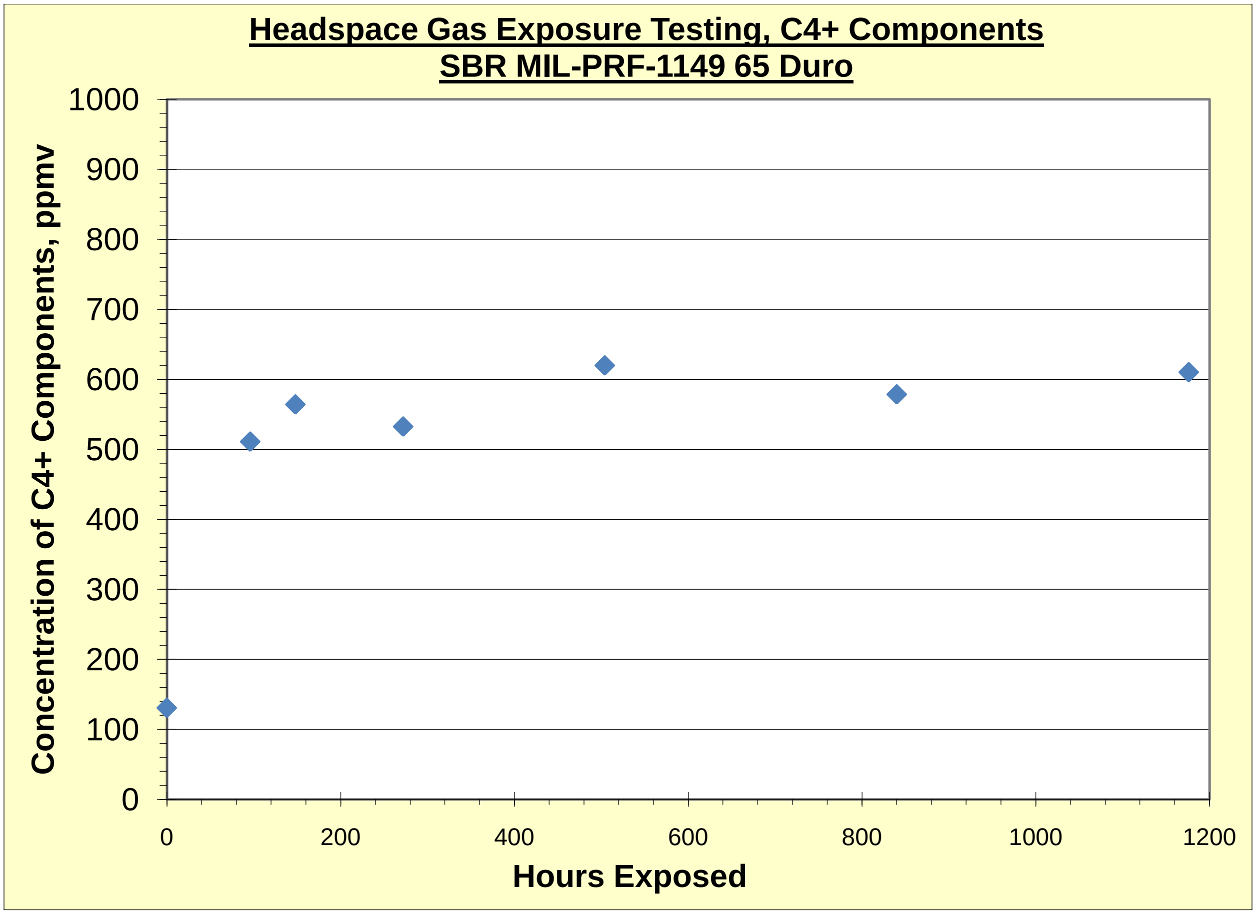

Figure 6. C4+ Head Space Test Results for SBR in Natural Gas Saturation Test

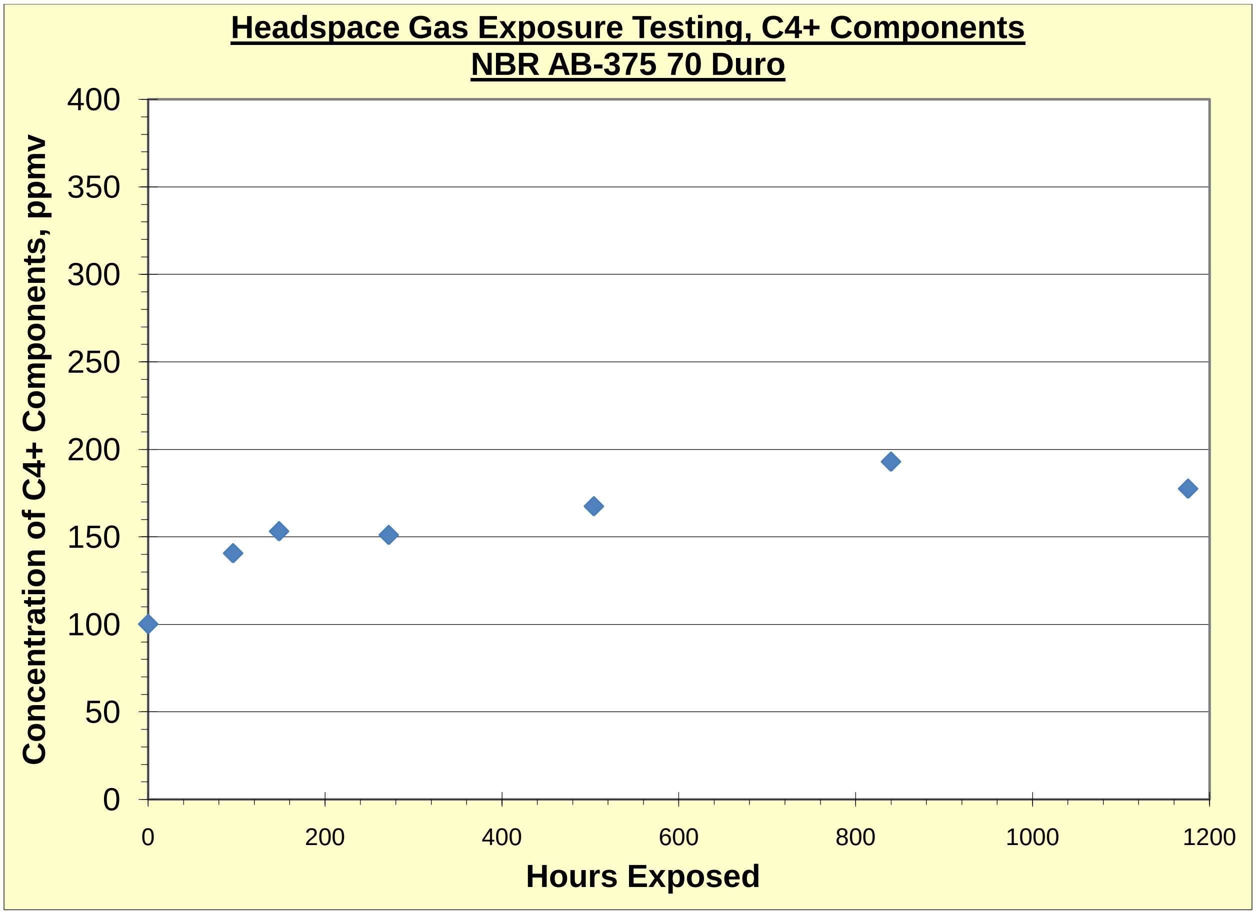

Figure 7. C4+ Head Space Test Results for NBR in Natural Gas Saturation Test

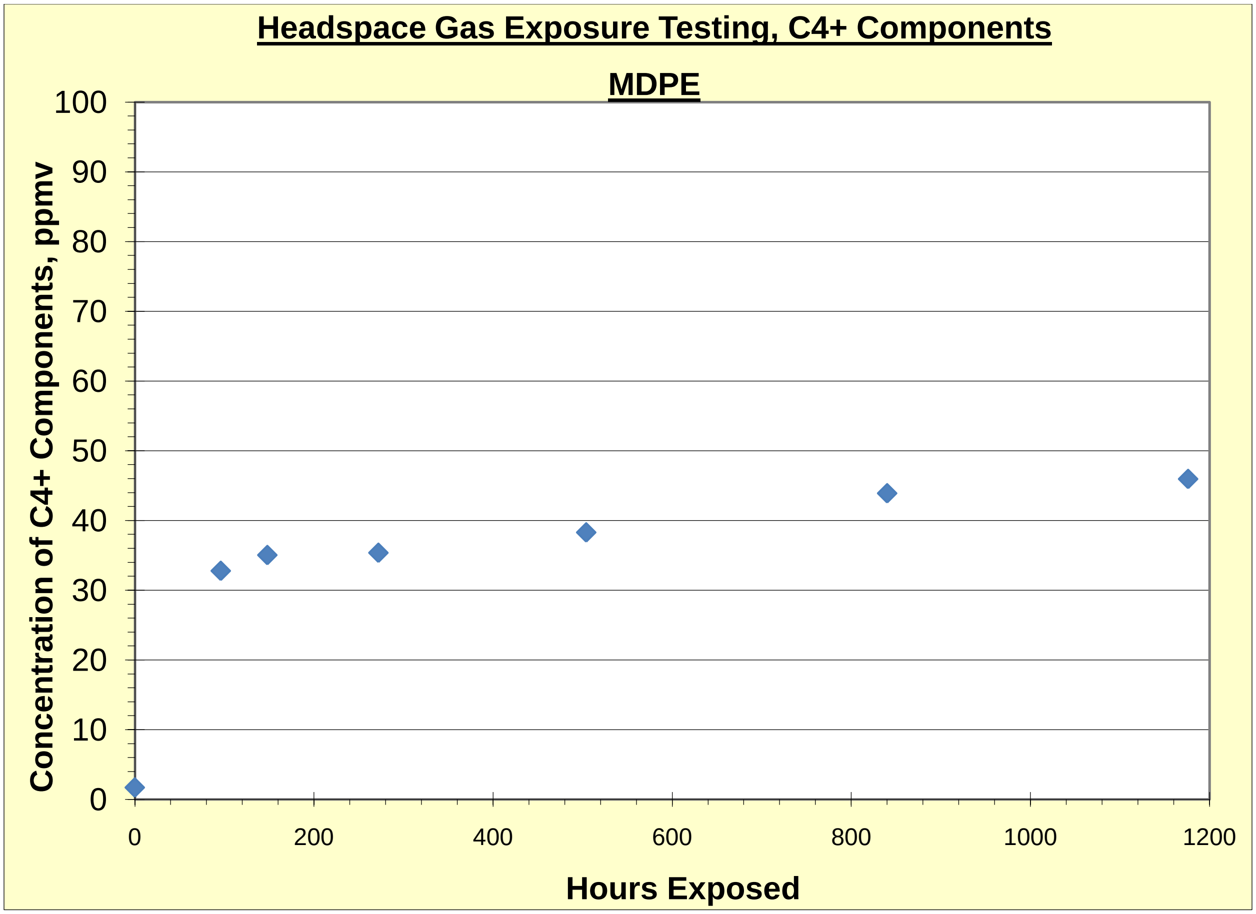

Figure 8. C4+ Head Space Test Results for MDPE in Natural Gas Saturation Test

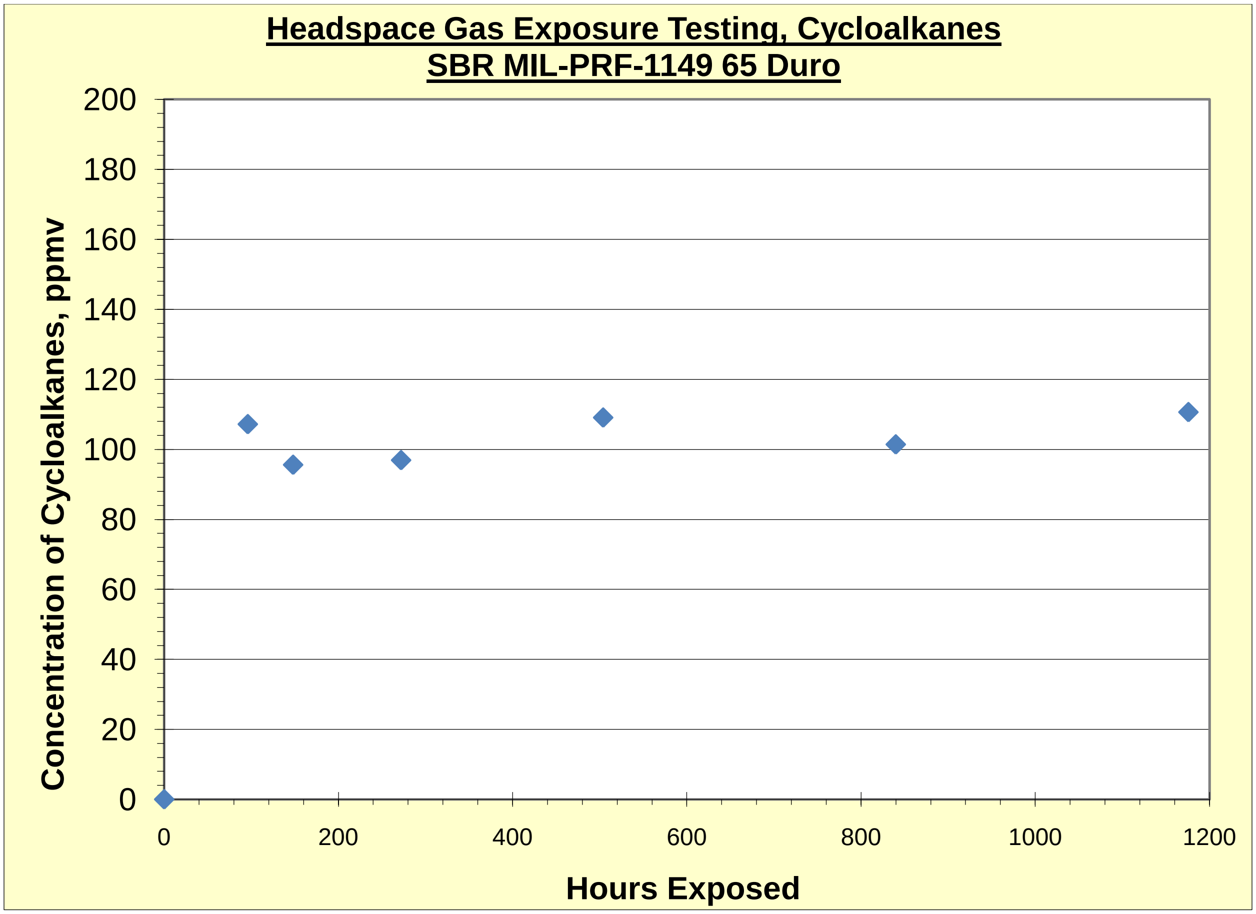

Figure 9. Cycloalkanes Head Space Test Results for SBR in Natural Gas Saturation Test

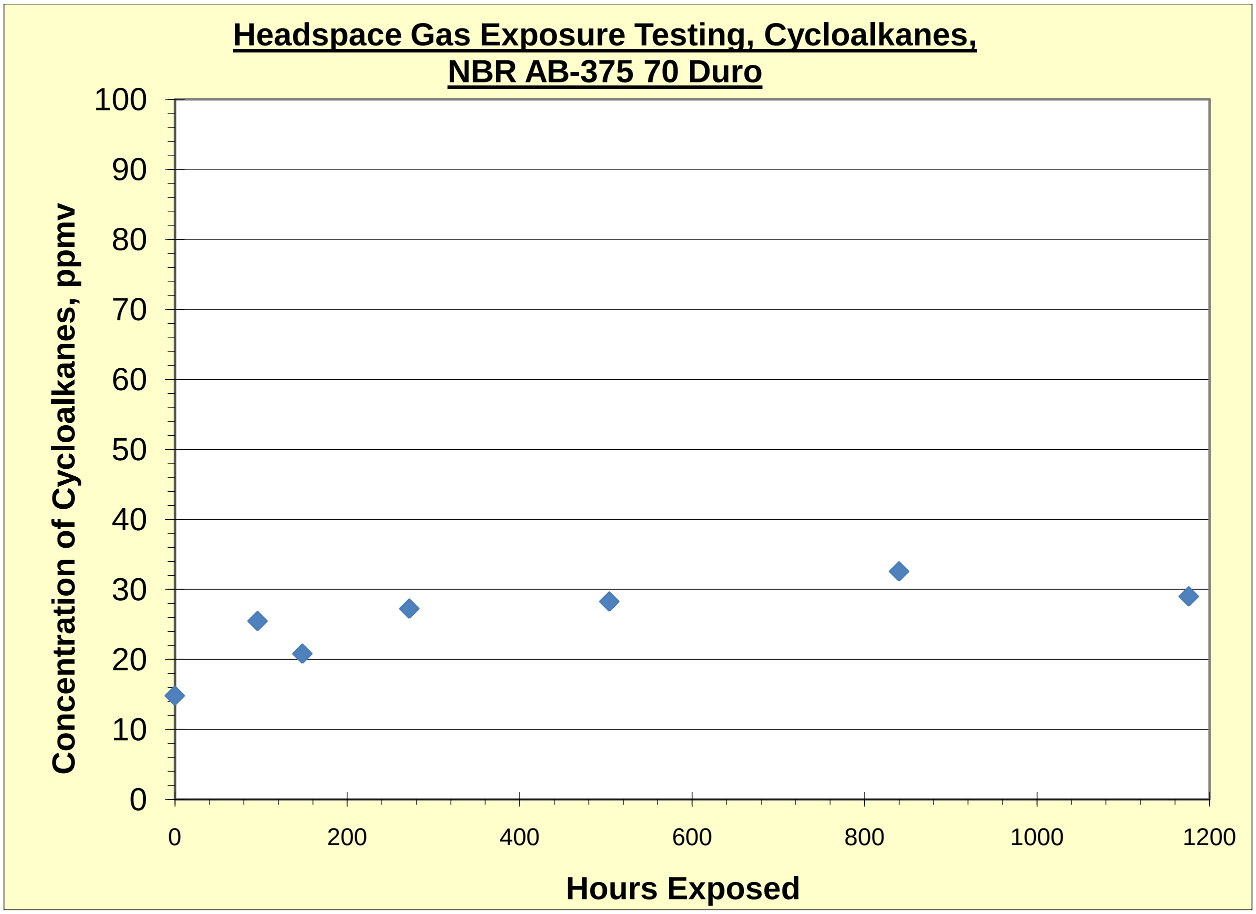

Figure 10. Cycloalkanes Head Space Test Results for NBR in Natural Gas Saturation Test

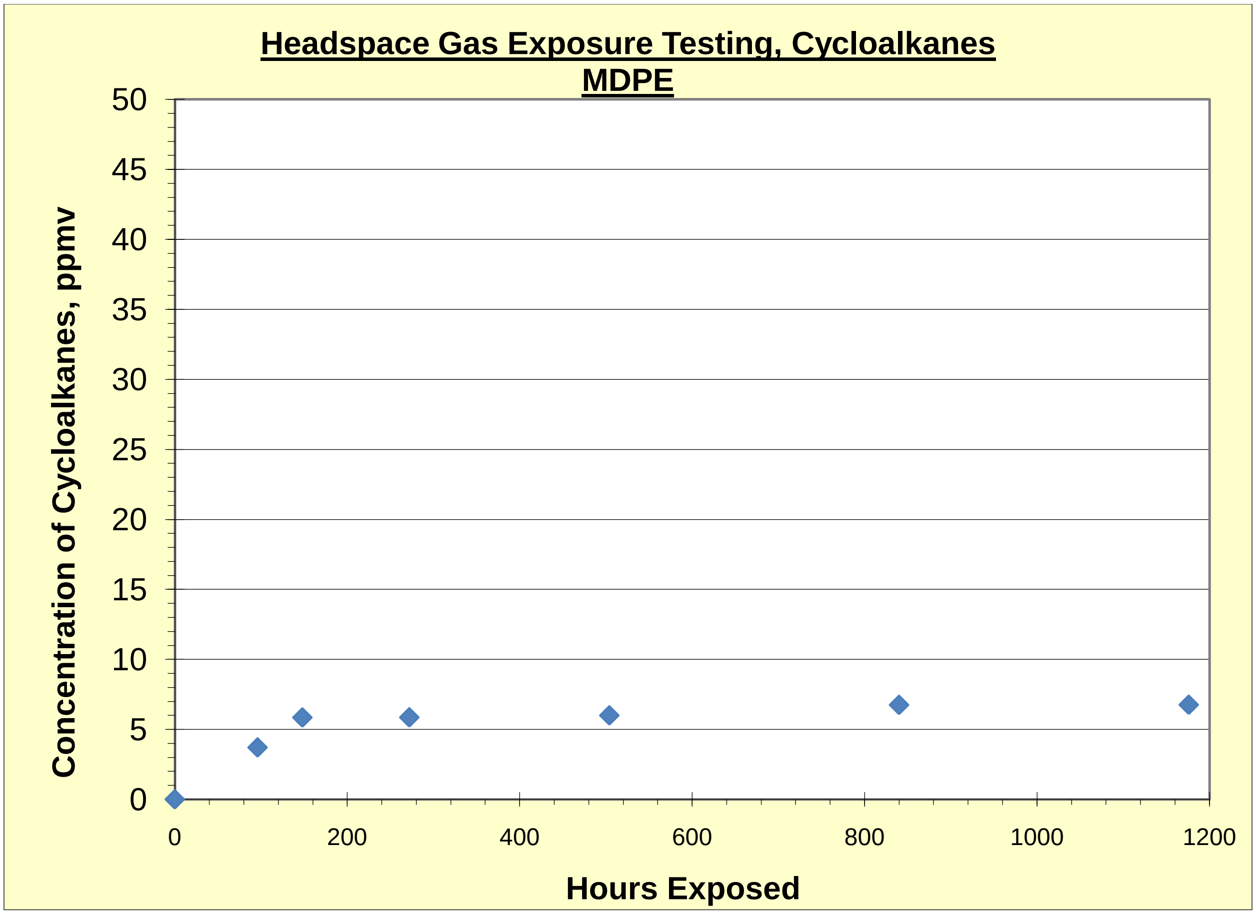

Figure 11. Cycloalkanes Head Space Test Results for MDPE in Natural Gas Saturation Test

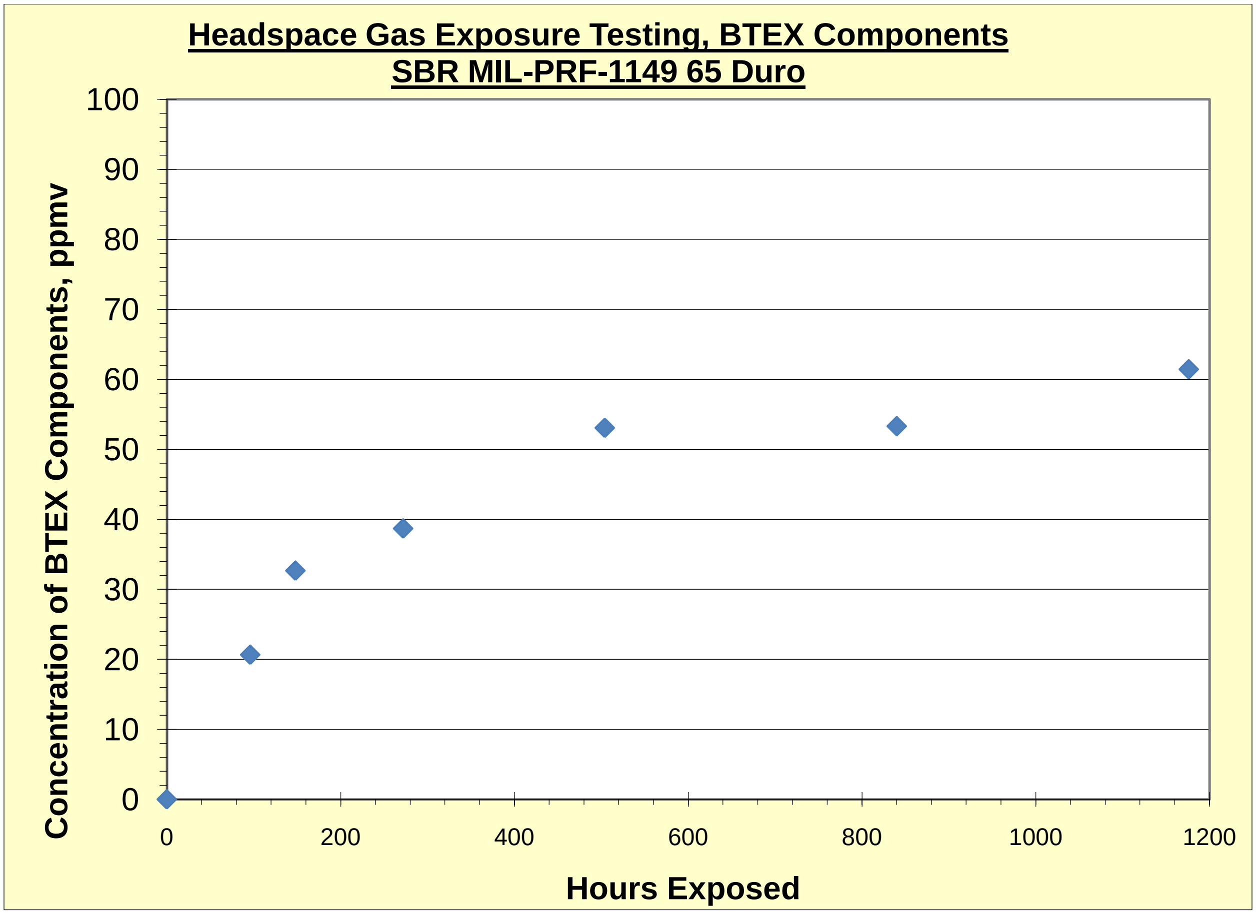

Figure 12. BTEX Head Space Test Results for SBR in Natural Gas Saturation Test

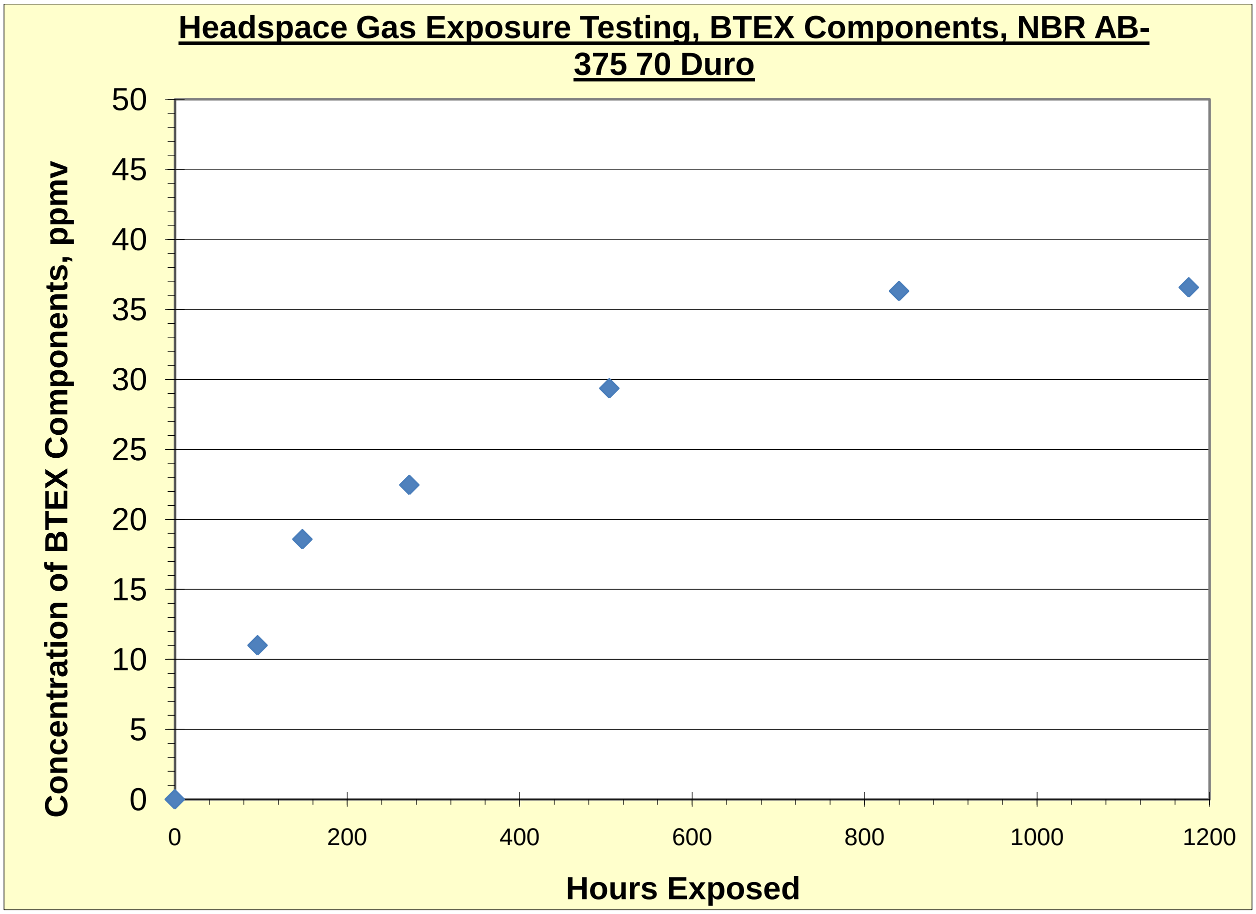

Figure 13. BTEX Head Space Test Results for NBR in Natural Gas Saturation Test

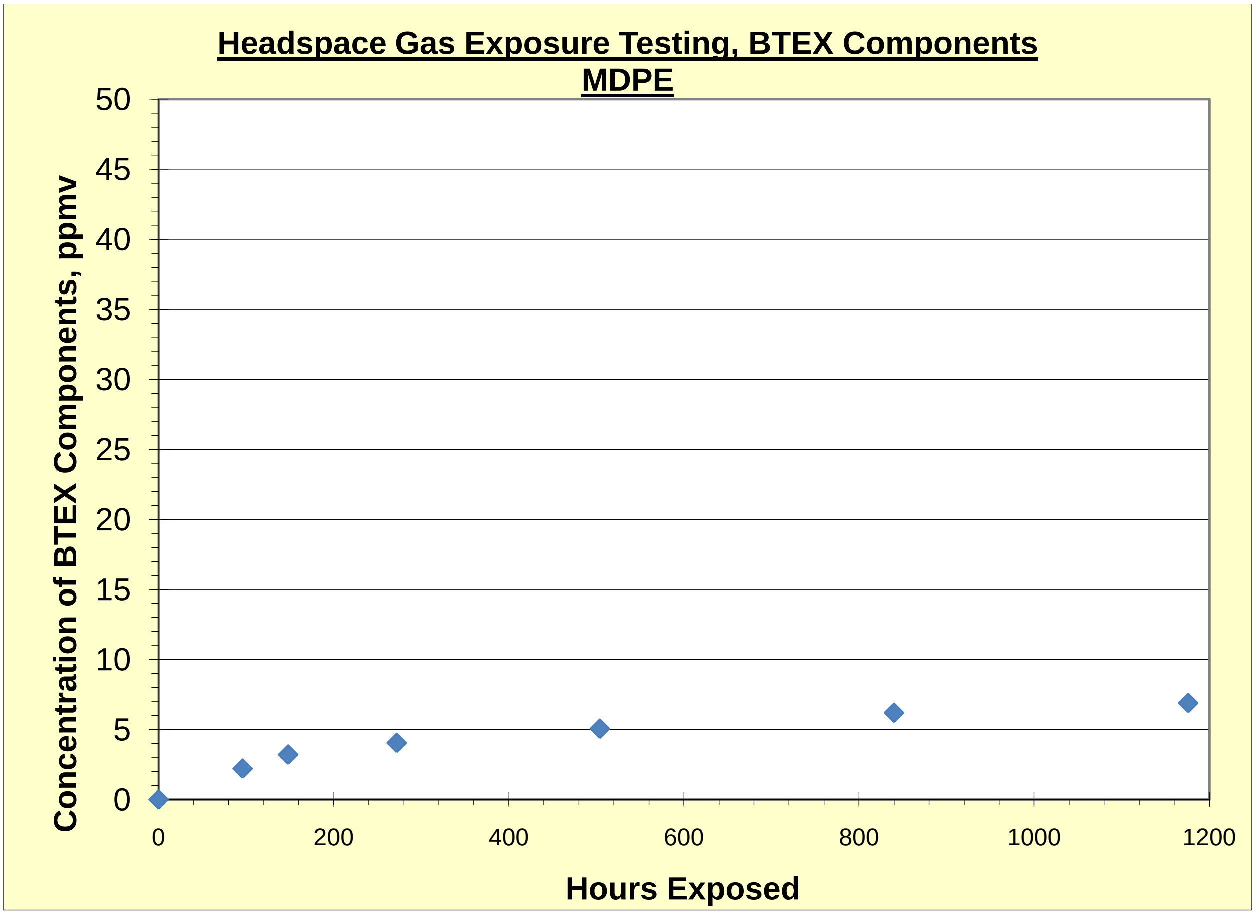

Figure 14. BTEX Head Space Test Results for MDPE in Natural Gas Saturation Test

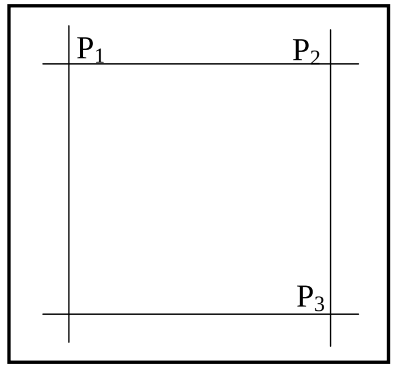

Figure 15. Dimensional Measurements on X (P_1P_2) and Y(P_2P_3) Directions